

Convergent Synthesis of Bis-1,2,4-triazinyl-2,2'-bipyridines (BTBPs) and Related Congeners via a Pd-catalyzed Ullman-type Reaction

Supporting Information

Gabrielle D. Waters and Jesse D. Carrick*

Department of Chemistry, Tennessee Tech University, 55 University Drive, Cookeville,
TN 38505-0001

<u>Table of Contents</u>	S1
Figure S1. Compound 10 ¹ H NMR	S2
Figure S2. Compound 10 ¹³ C NMR	S3
Figure S3. Compound 11 ¹ H NMR	S4
Figure S4. Compound 11 ¹³ C NMR	S5
Figure S5. Compound 12 ¹ H NMR	S6
Figure S6. Compound 12 ¹³ C NMR	S7
Figure S7. Compound 13 ¹ H NMR	S8
Figure S8. Compound 13 ¹³ C NMR	S9
Figure S9. Compound 14 ¹ H NMR	S10
Figure S10. Compound 14 ¹³ C NMR	S11
Figure S11. Compound 15 ¹ H NMR	S12
Figure S12. Compound 15 ¹³ C NMR	S13
Figure S13. Chromatogram of 10	S14
Figure S14. Chromatogram of 11	S15
Figure S15. Chromatogram of 12	S16
Figure S16. Chromatogram of 13	S17
Figure S17. Chromatogram of 14	S18
Figure S18. Chromatogram of 15	S19

Figure S1. ^1H NMR Spectrum of Compound **10** (CDCl_3)

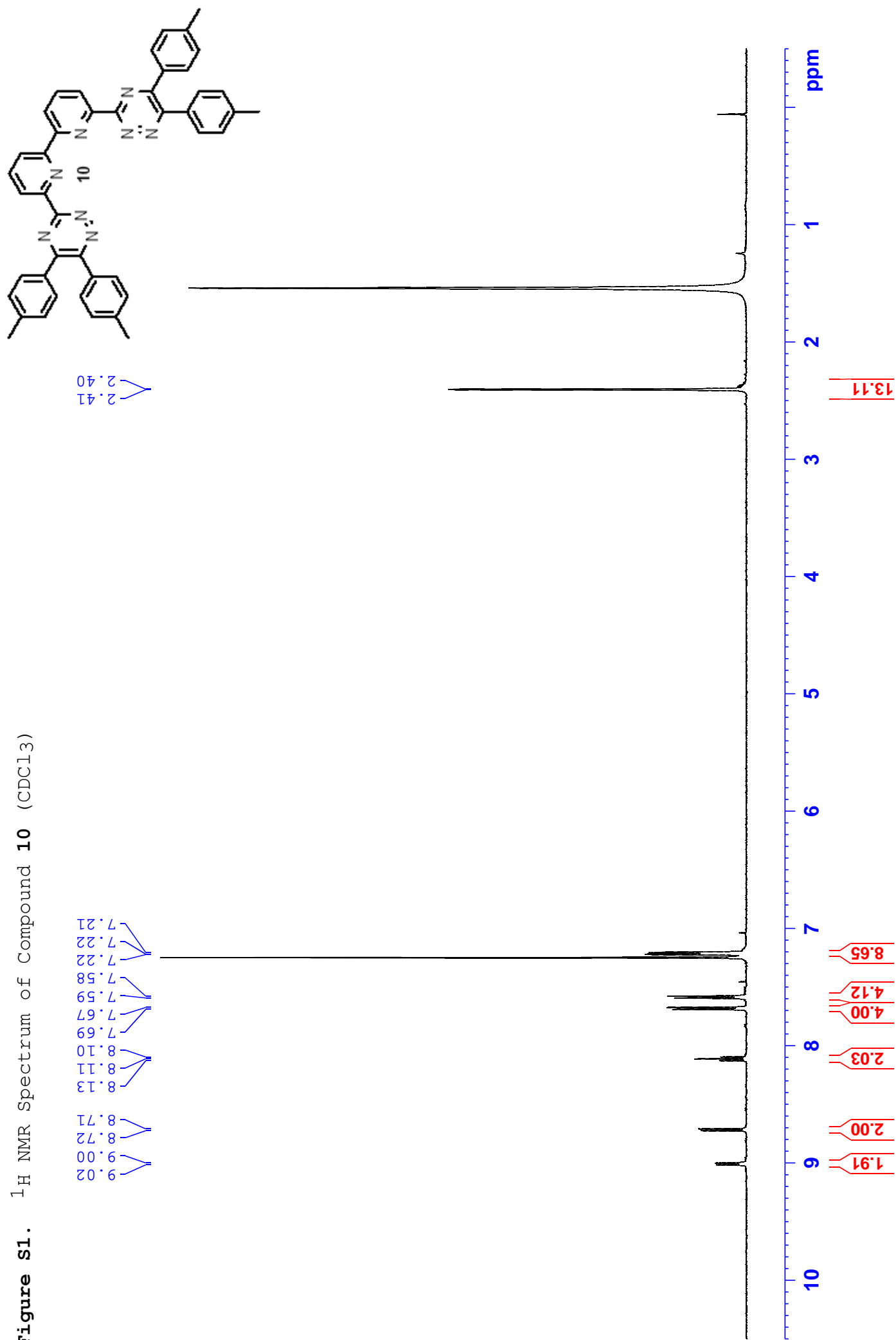


Figure S2. ^{13}C NMR of Compound **10** (CDCl_3)

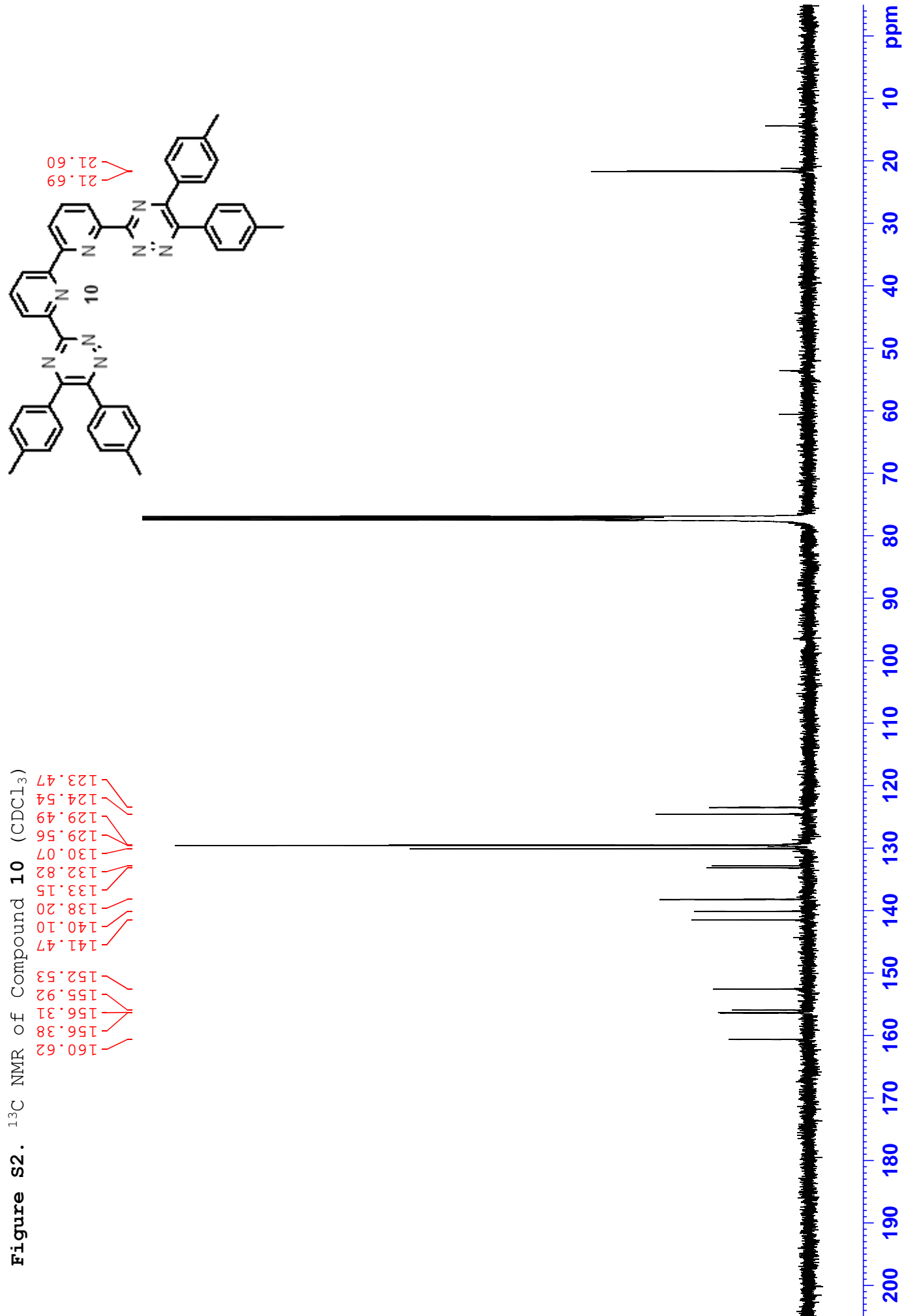


Figure S3. ^1H NMR spectrum of **11** [$(\text{CD}_3)_2\text{SO}$]

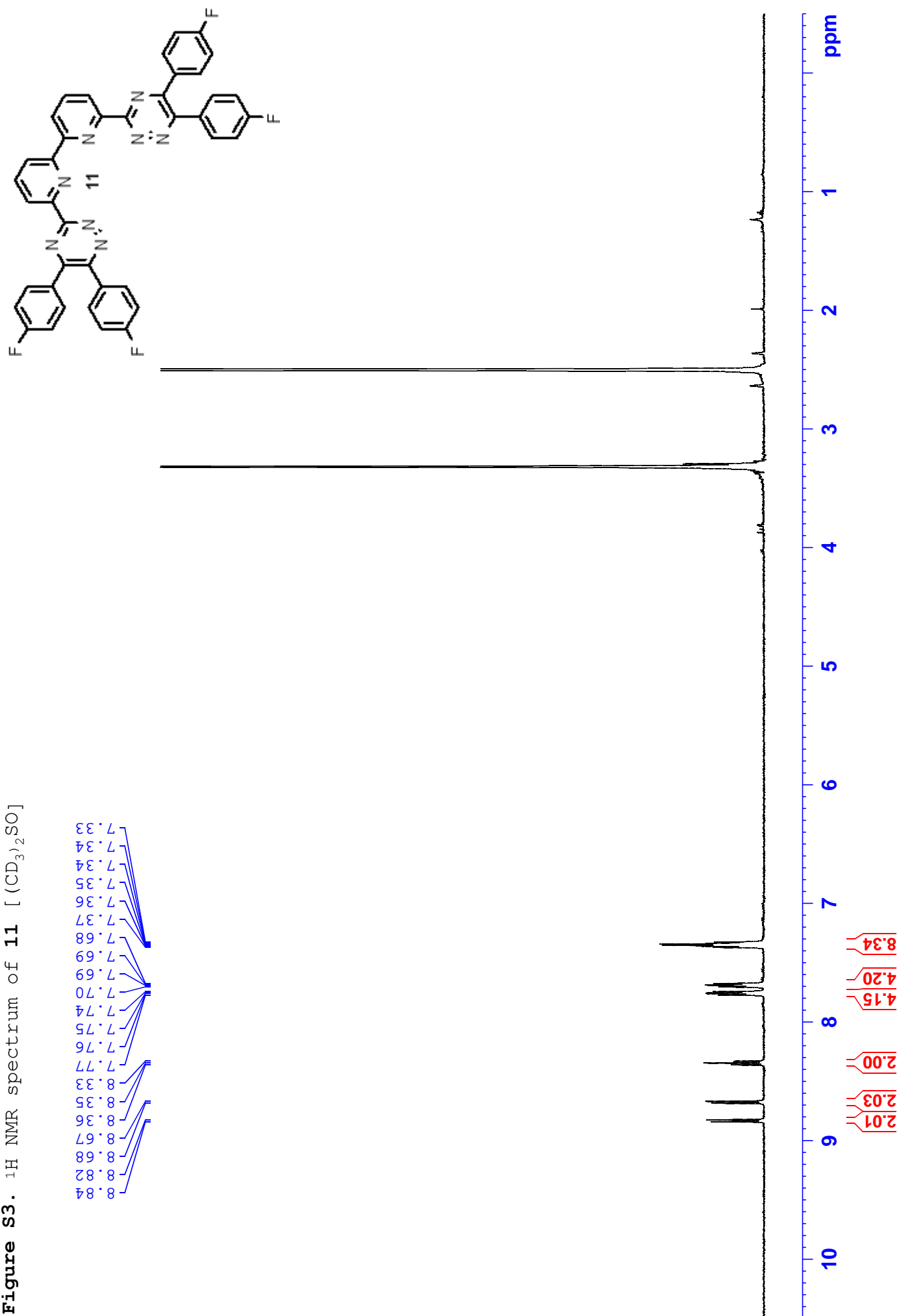
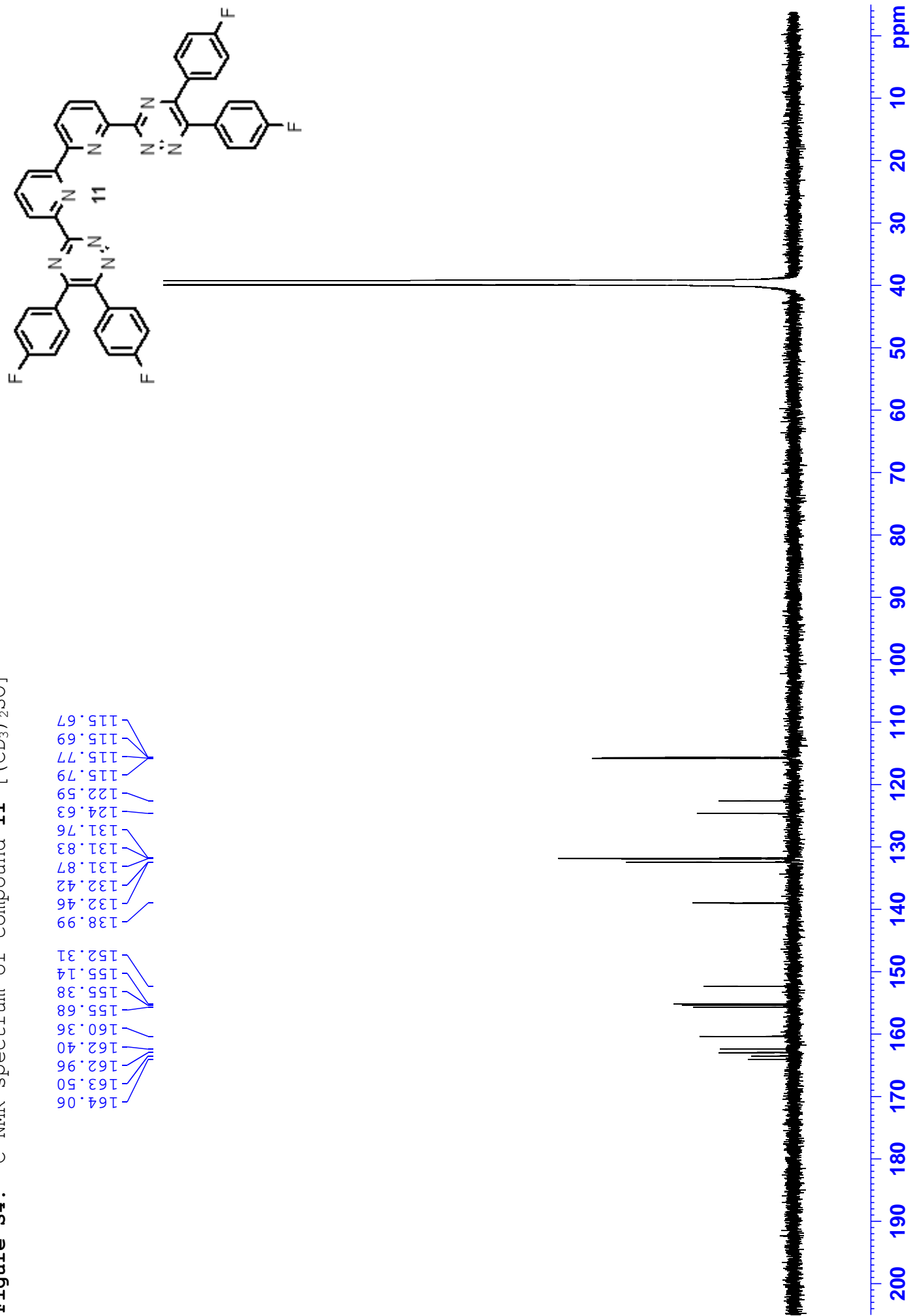


Figure S4. ¹³C NMR spectrum of compound **11** [(CD₃)₂SO]



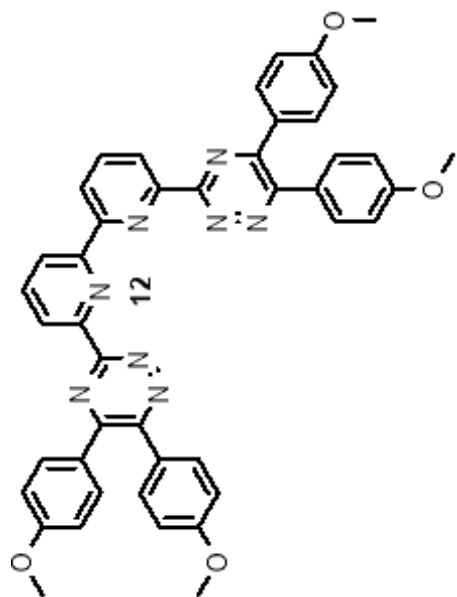


Figure S5. ^1H NMR spectrum of compound **12** (CDCl_3)

9.034
 9.019
 8.734
 8.719
 8.144
 8.129
 8.114
 7.810
 7.793
 7.687
 7.670
 6.964
 6.944
 6.926
 3.877
 3.870

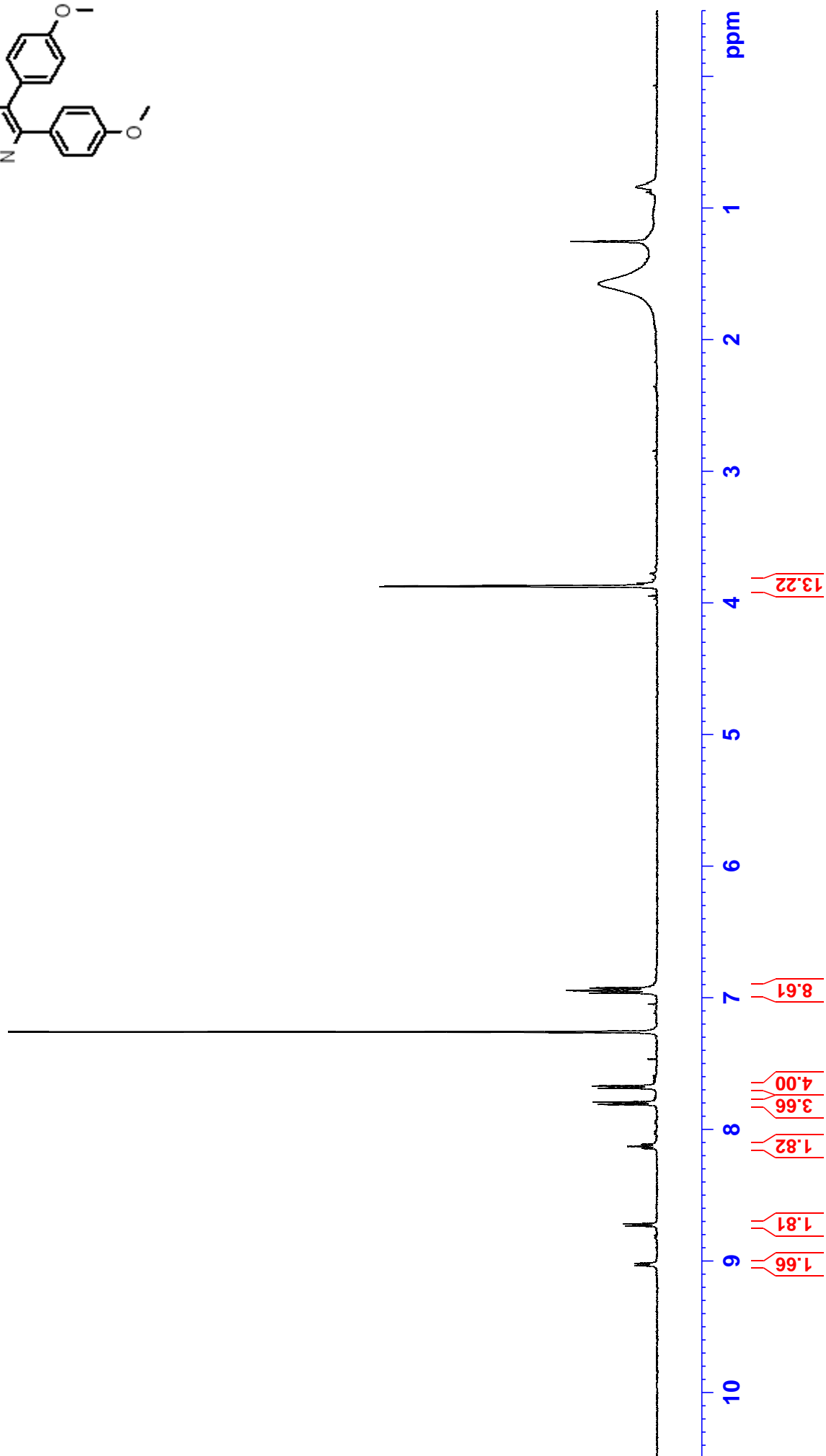


Figure S6. ^{13}C NMR spectrum of compound **12** (CDCl_3)

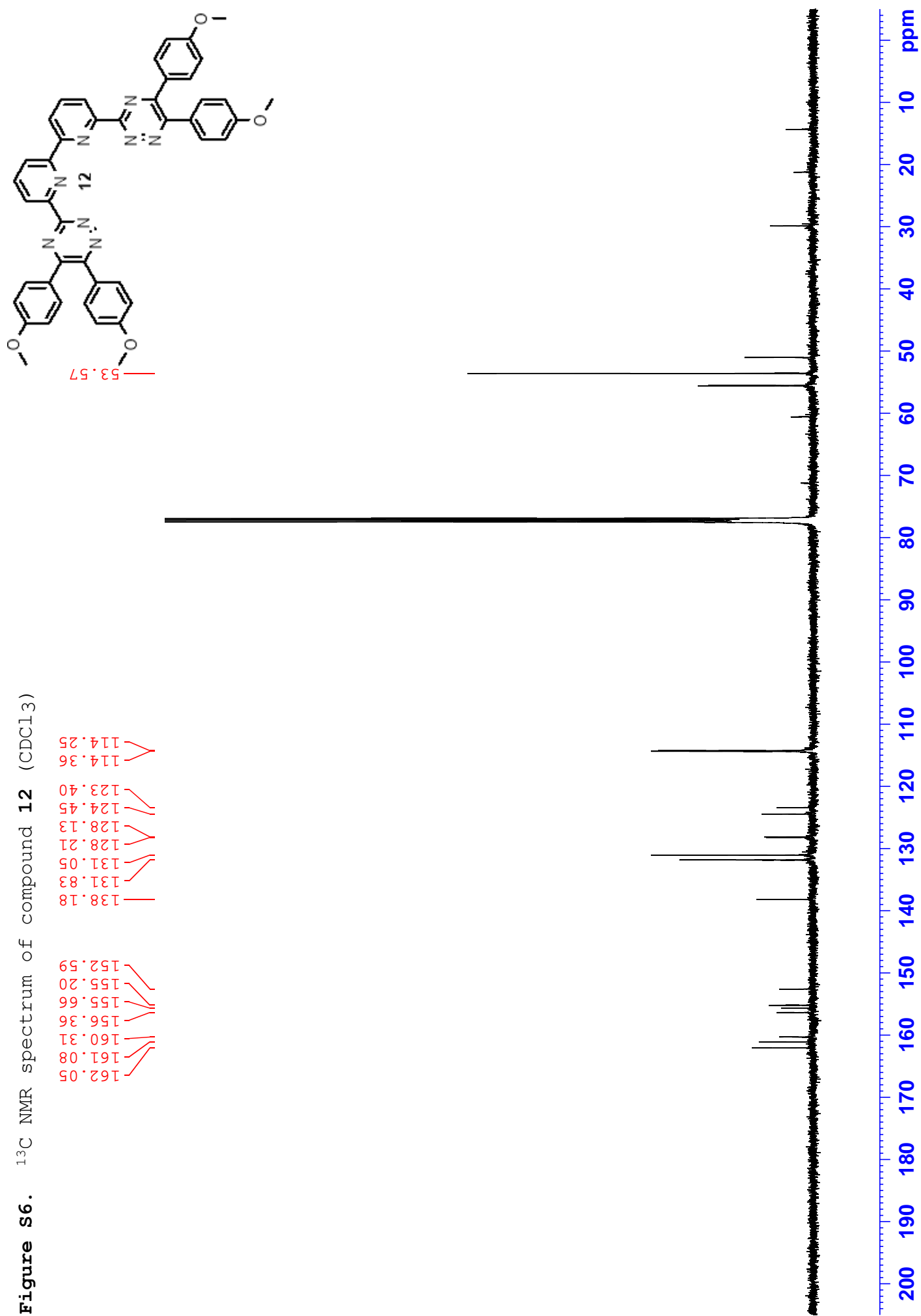
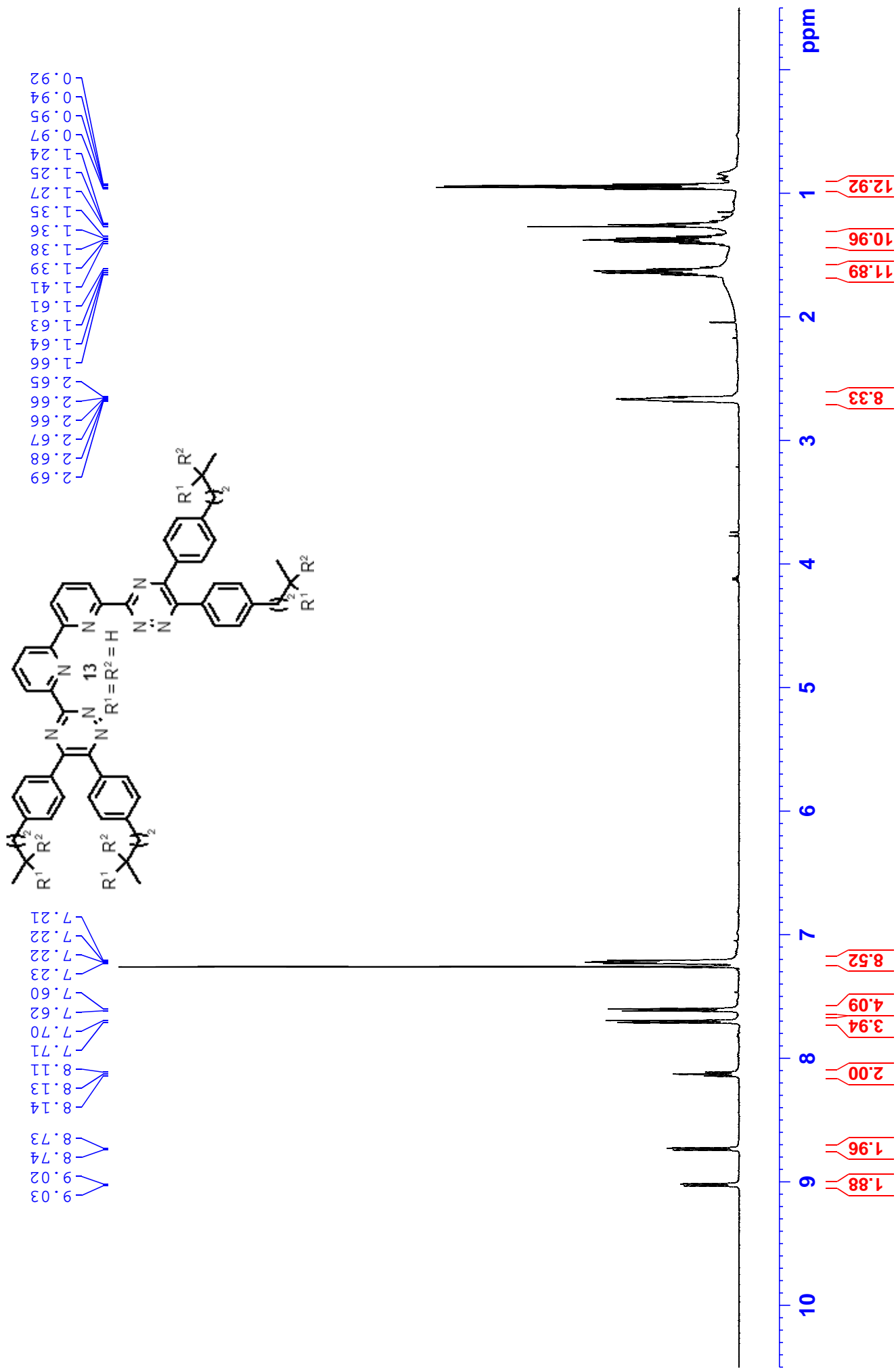


Figure S7. ¹H NMR spectrum of compound **13** (CDCl₃)



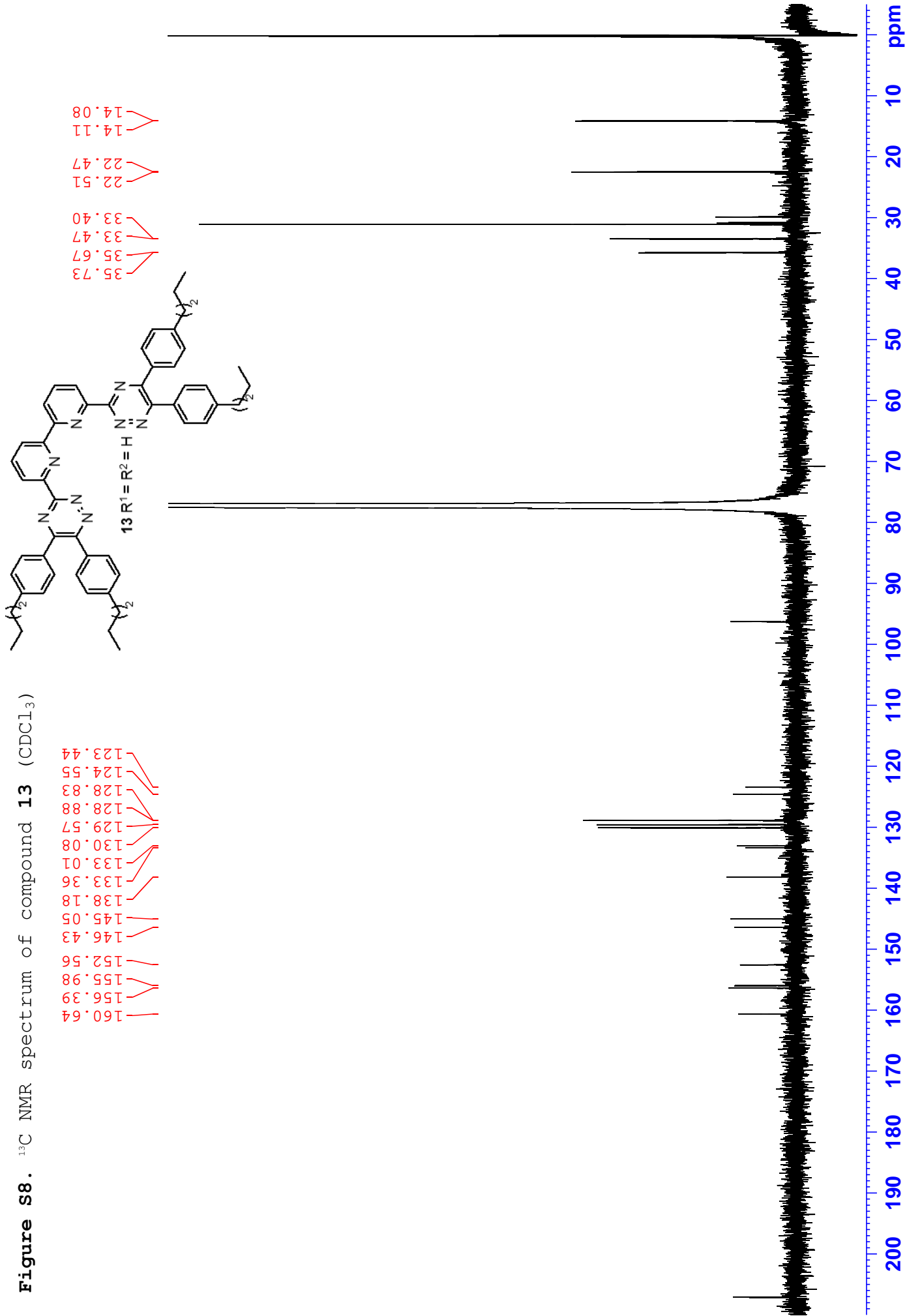


Figure S9. ¹H NMR spectrum of compound 14 (CDCl₃)

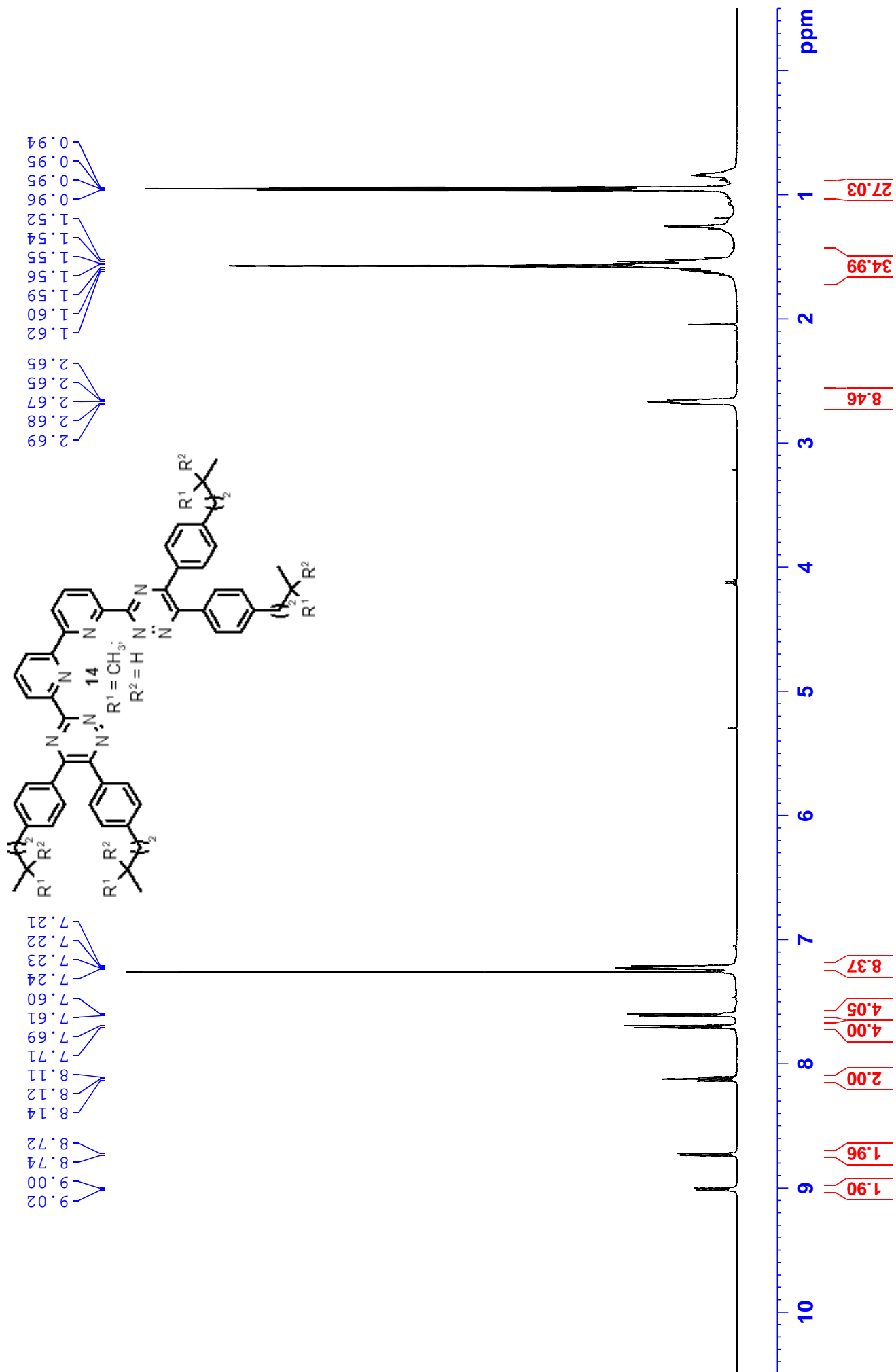


Figure S10. ^{13}C NMR spectrum of compound **14** (CDCl_3)

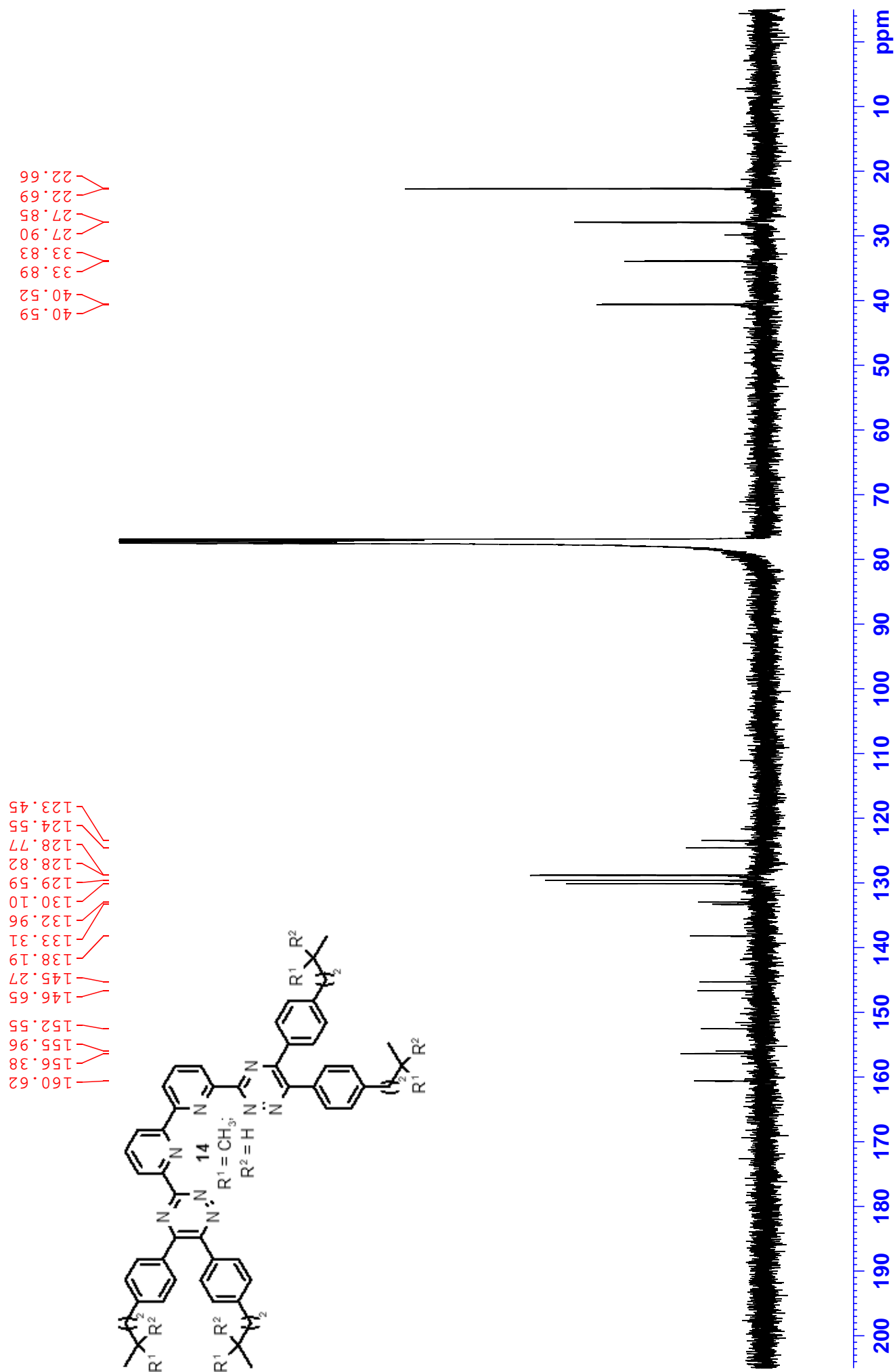


Figure 11. ¹H NMR spectrum of compound **15** (CDCl₃)

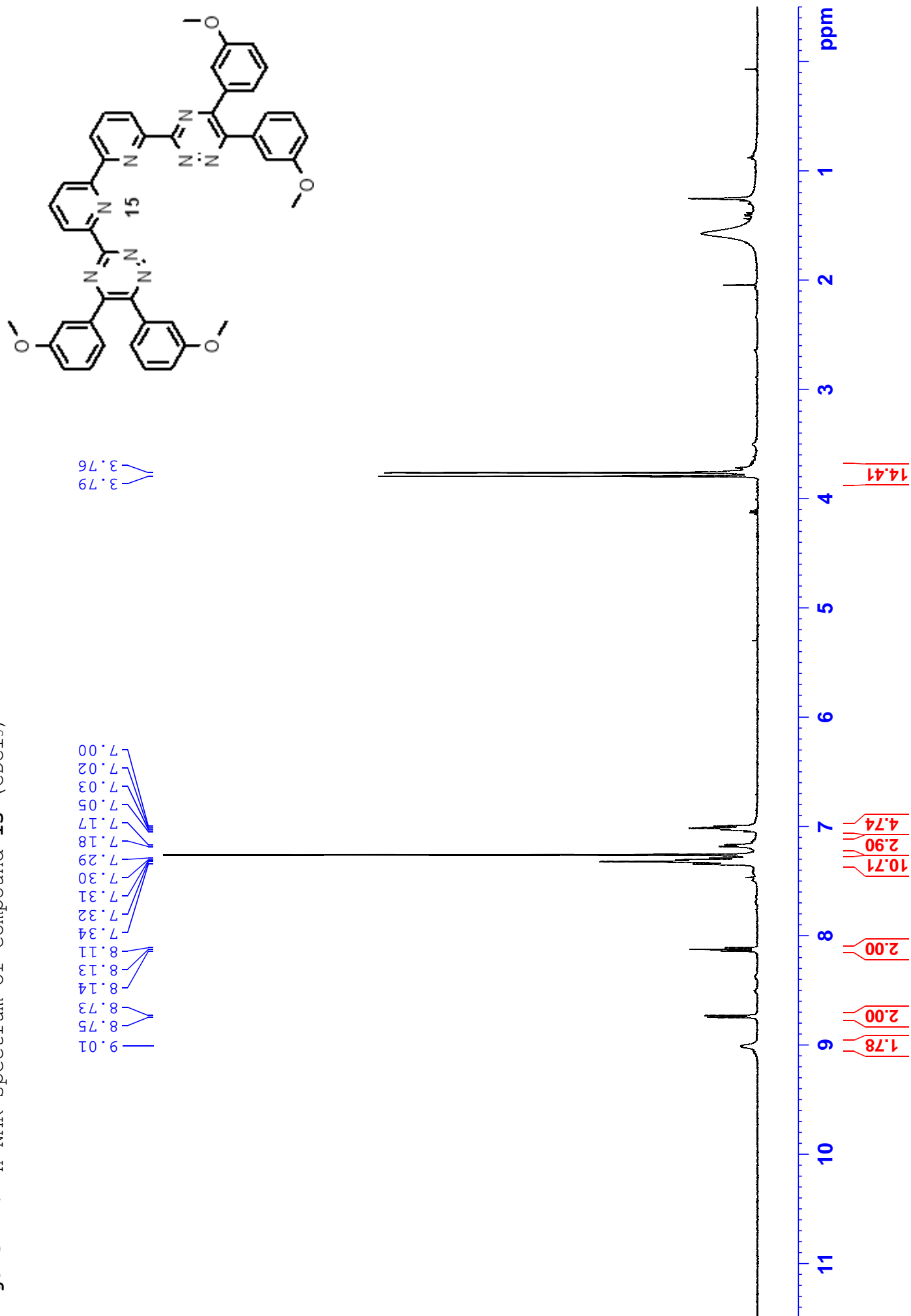


Figure S12. ¹³C NMR spectrum of compound **15** (CDCl₃)

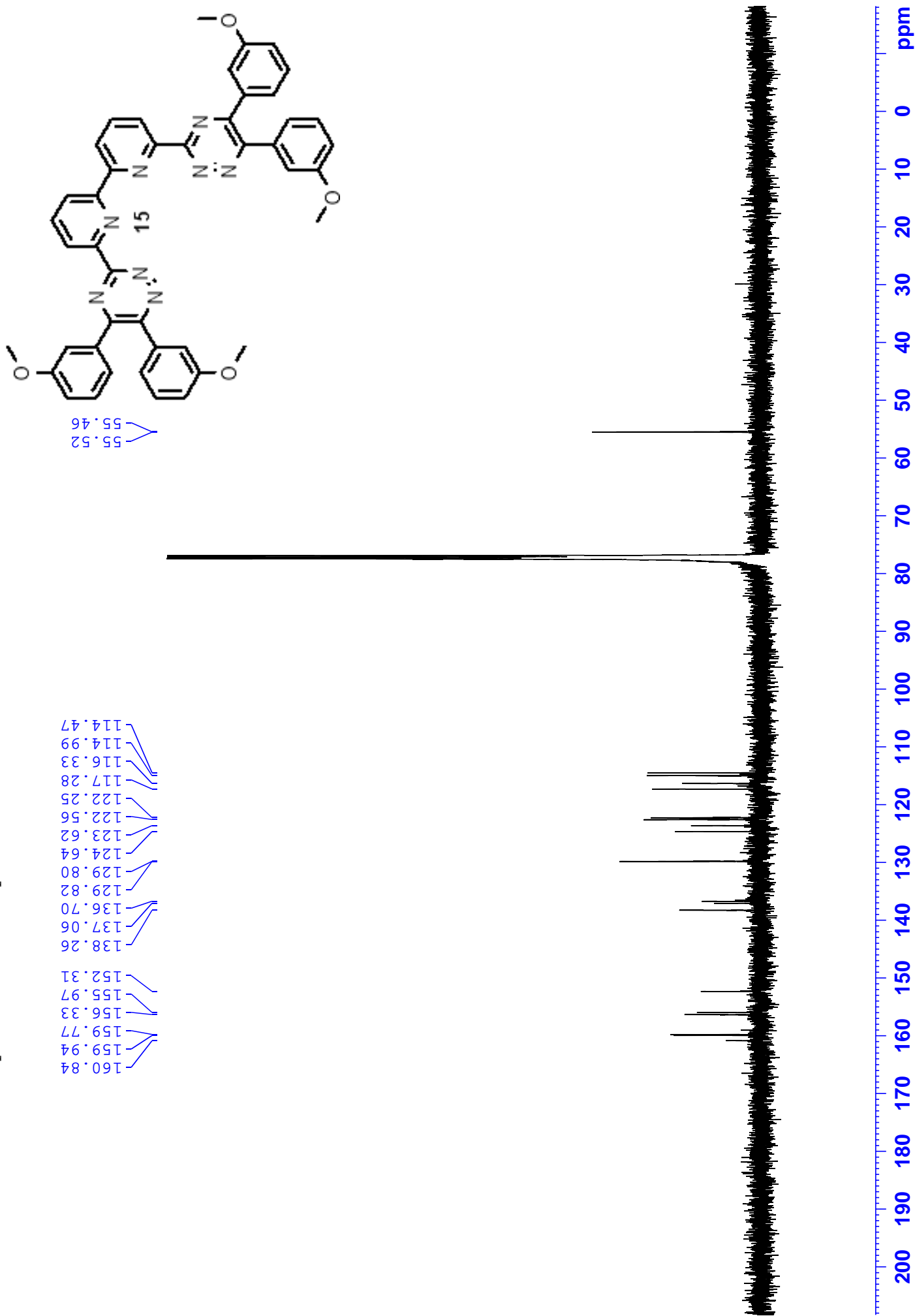


Figure S13.

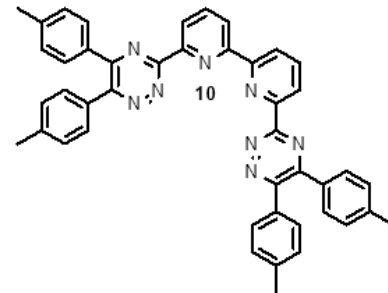
Sample: GDW-B-243-1

Rf 200

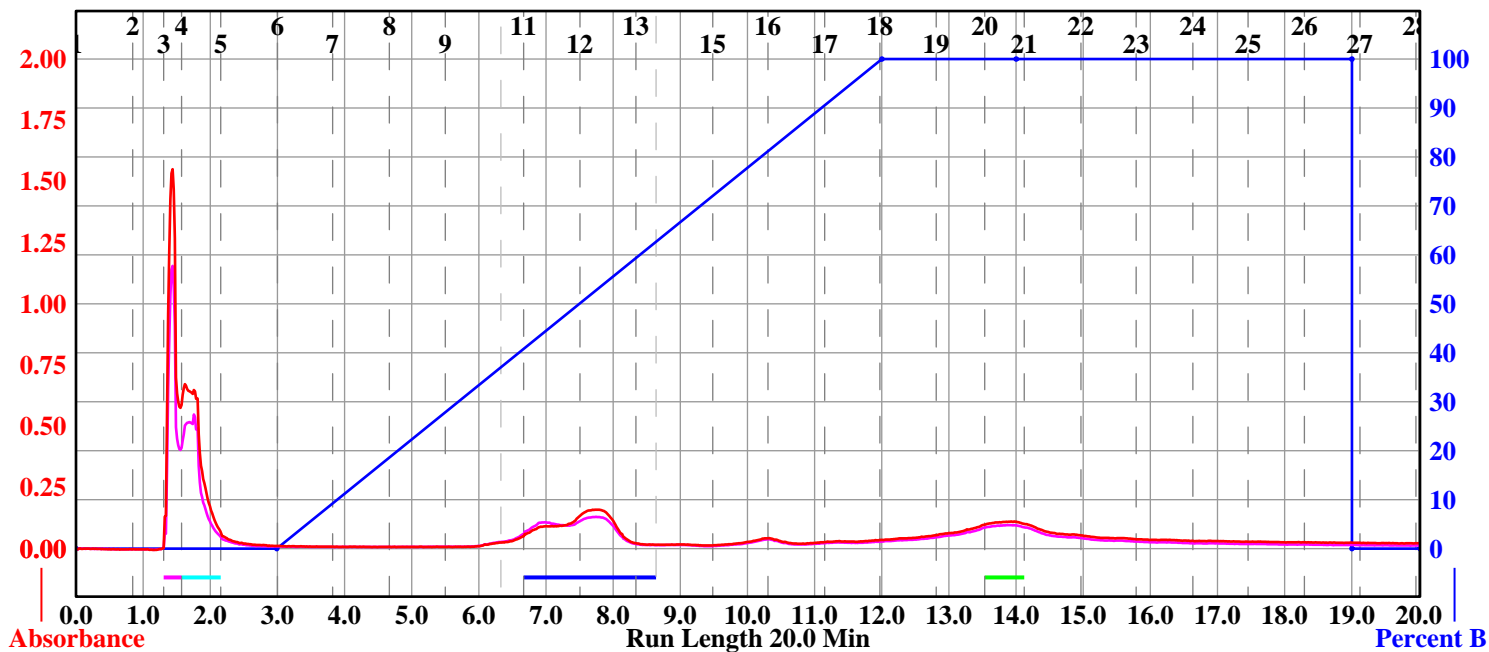
Monday 18 March 2019 03:05PM

4x Column: 4
 RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A1 hexane
 Solvent: B1 ethyl acetate

Peak Tube Volume: 15 ml
 Non-Peak Tube Volume: 15 ml
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm



Run Notes: 6,6'-bis-[5,6-bis(4-methylphenyl)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (10)



Rack A				
70	69	68	67	66
61	62	63	64	65
60	59	58	57	56
51	52	53	54	55
50	49	48	47	46
41	42	43	44	45
40	39	38	37	36
31	32	33	34	35
30	29	28	27	26
21	22	23	24	25
20	19	18	17	16
11	12	13	14	15
10	9	8	7	6
1	2	3	4	5

18 mm x 150 mm Tubes

Peak #	Start Tube	End Tube
1	A:3	A:3
2	A:4	A:4
3	A:11	A:13
4	A:20	A:20

Duration	%B	Solvent A	Solvent B
0.0	0.0	A1 hexane	B1 ethyl acetate
3.0	0.0	A1 hexane	B1 ethyl acetate
9.0	100.0	A1 hexane	B1 ethyl acetate
2.0	100.0	A1 hexane	B1 ethyl acetate
5.0	100.0	A1 hexane	B1 ethyl acetate
0.0	0.0	A1 hexane	B1 ethyl acetate
1.0	0.0	A1 hexane	B1 ethyl acetate

Figure S14.

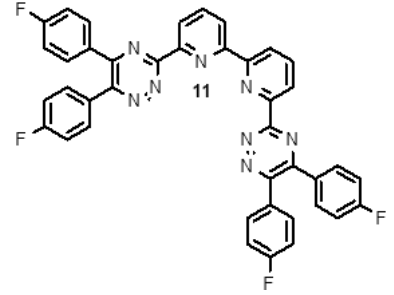
Sample: GDW-C-51-1

Rf 200

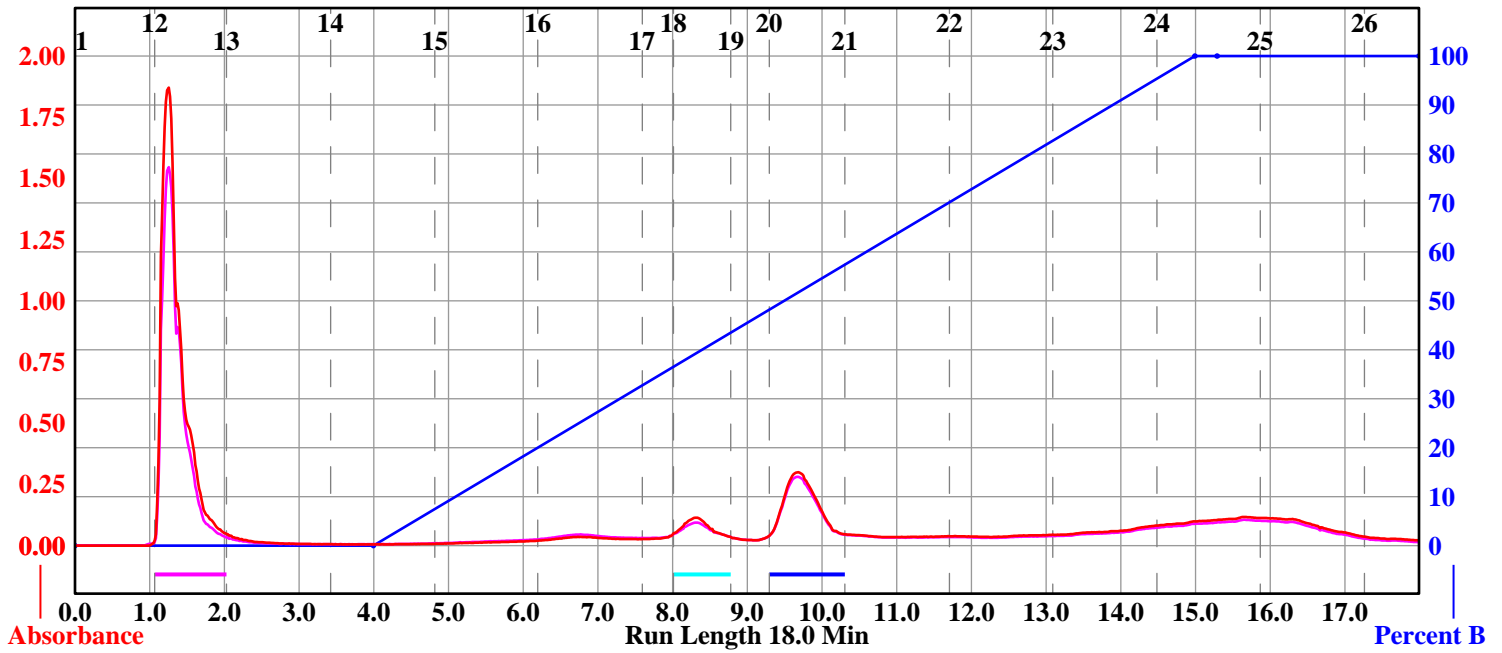
Tuesday 04 June 2019 10:46AM

RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A1 hexane
 Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
 Non-Peak Tube Volume: Max.
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm



Run Notes: 6,6'-bis-[5,6-bis(4-fluoro)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (11)



Rack A				
70	69	68	67	66
61	62	63	64	65
60	59	58	57	56
51	52	53	54	55
50	49	48	47	46
41	42	43	44	45
40	39	38	37	36
31	32	33	34	35
30	29	28	27	26
21	22	23	24	25
20	19	18	17	16
11	12	13	14	15
10	9	8	7	6
1	2	3	4	5

18 mm x 150 mm Tubes

Peak #	Start Tube	End Tube
1	A:12	A:12
2	A:18	A:18
3	A:20	A:20

Duration	%B	Solvent A	Solvent B
0.0	0.0	A1 hexane	B1 ethyl acetate
4.0	0.0	A1 hexane	B1 ethyl acetate
11.0	100.0	A1 hexane	B1 ethyl acetate
0.3	100.0	A1 hexane	B1 ethyl acetate
2.7	100.0	A1 hexane	B1 ethyl acetate

Figure S15.

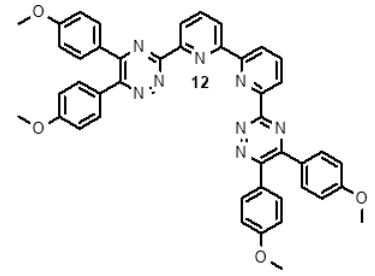
Sample: GDW-C-129-1

Rf 200

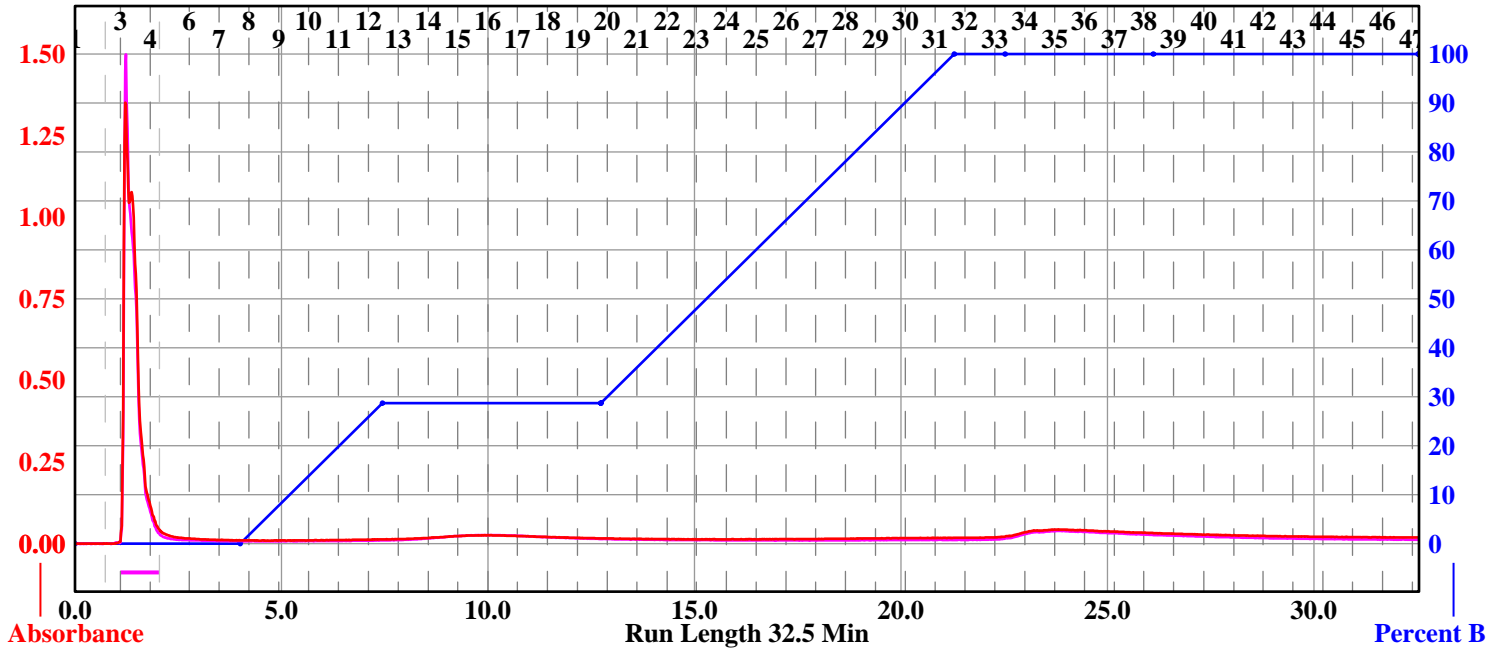
Monday 15 July 2019 04:57PM

RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A2 dichloromethane
 Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
 Non-Peak Tube Volume: Max.
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm



Run Notes: 6,6'-bis-[5,6-bis(4-methoxy)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (12)



Rack A				
71	72	73	74	75
70	69	68	67	66
61	62	63	64	65
60	59	58	57	56
51	52	53	54	55
50	49	48	47	46
41	42	43	44	45
40	39	38	37	36
31	32	33	34	35
30	29	28	27	26
21	22	23	24	25
20	19	18	17	16
11	12	13	14	15
10	9	8	7	6
1	2	3	4	5

16 mm x 100 mm Tubes

Peak #	Start Tube	End Tube
1	A:3	A:4

Duration	%B	Solvent A	Solvent B
0.0	0.0	A2 dichlorometha	B1 ethyl acetate
4.0	0.0	A2 dichlorometha	B1 ethyl acetate
3.4	28.7	A2 dichlorometha	B1 ethyl acetate
5.3	28.7	A2 dichlorometha	B1 ethyl acetate
0.0	28.7	A2 dichlorometha	B1 ethyl acetate
8.6	100.0	A2 dichlorometha	B1 ethyl acetate
1.2	100.0	A2 dichlorometha	B1 ethyl acetate
3.6	100.0	A2 dichlorometha	B1 ethyl acetate
6.4	100.0	A2 dichlorometha	B1 ethyl acetate
0.0	100.0	A2 dichlorometha	B1 ethyl acetate

Figure S16.

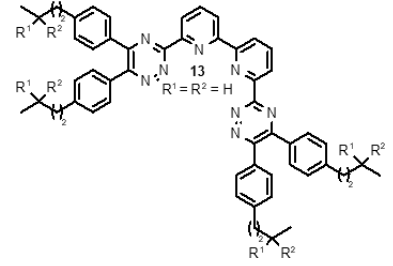
Sample: GDW-C-229-1

Rf 200

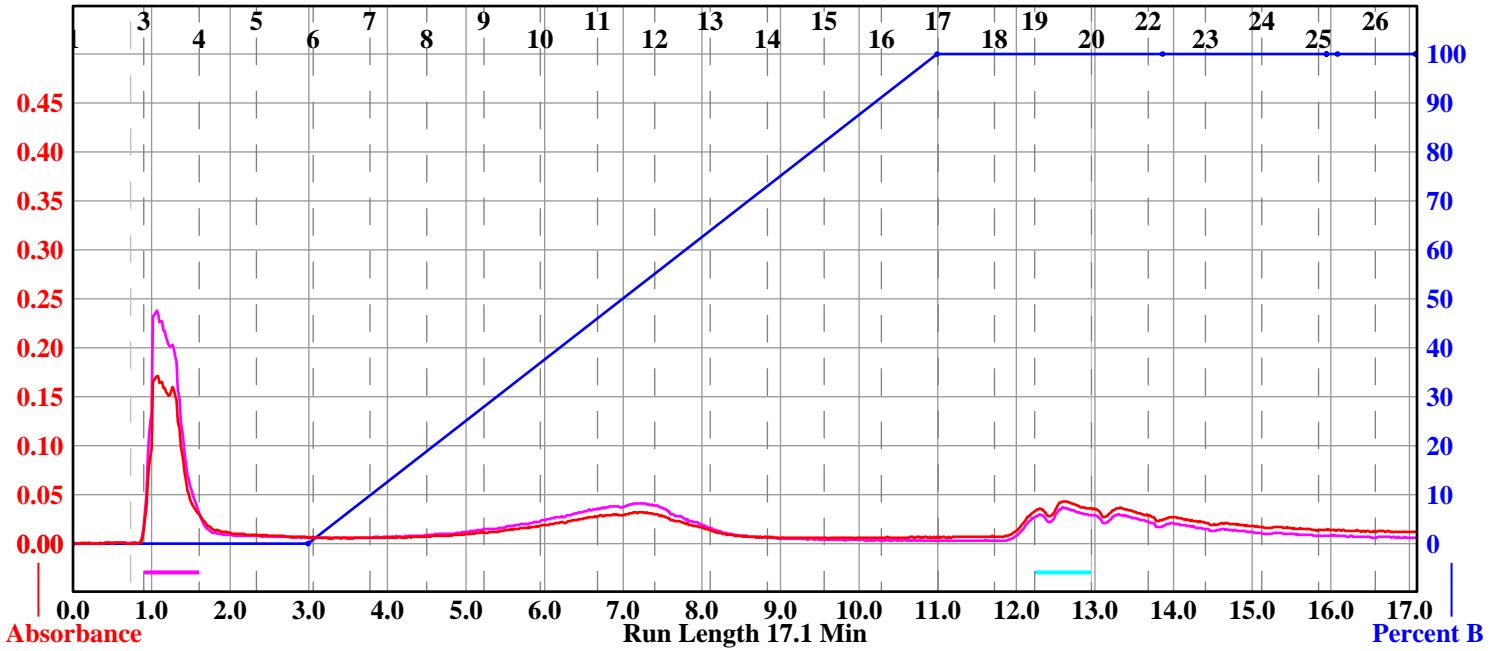
Friday 30 August 2019 03:39PM

RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A2 dichloromethane
 Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
 Non-Peak Tube Volume: Max.
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm



Run Notes: 6,6'-bis-[5,6-bis(4-butylphenyl)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (13)



Rack A					Peak #	Start Tube	End Tube
(71)	(72)	(73)	(74)	(75)	1	A:3	A:3
(70)	(69)	(68)	(67)	(66)	2	A:19	A:20
(61)	(62)	(63)	(64)	(65)			
(60)	(59)	(58)	(57)	(56)			
(51)	(52)	(53)	(54)	(55)			
(50)	(49)	(48)	(47)	(46)			
(41)	(42)	(43)	(44)	(45)			
(40)	(39)	(38)	(37)	(36)			
(31)	(32)	(33)	(34)	(35)			
(30)	(29)	(28)	(27)	(26)			
(21)	(22)	(23)	(24)	(25)			
(20)	(19)	(18)	(17)	(16)			
(11)	(12)	(13)	(14)	(15)			
(10)	(9)	(8)	(7)	(6)			
(1)	(2)	(3)	(4)	(5)			

Duration	%B	Solvent A	Solvent B
0.0	0.0	A2 dichlorometha	B1 ethyl acetate
3.0	0.0	A2 dichlorometha	B1 ethyl acetate
8.0	100.0	A2 dichlorometha	B1 ethyl acetate
2.9	100.0	A2 dichlorometha	B1 ethyl acetate
2.1	100.0	A2 dichlorometha	B1 ethyl acetate
0.0	100.0	A2 dichlorometha	B1 ethyl acetate
0.1	100.0	A2 dichlorometha	B1 ethyl acetate
1.0	100.0	A2 dichlorometha	B1 ethyl acetate
0.0	100.0	A2 dichlorometha	B1 ethyl acetate

16 mm x 100 mm Tubes

Figure S17.

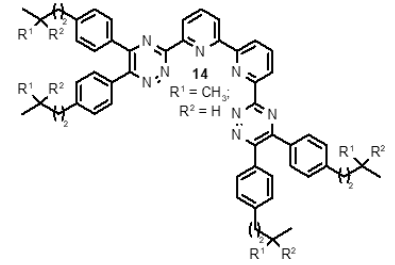
Sample: GDW-C-139-1

Rf 200

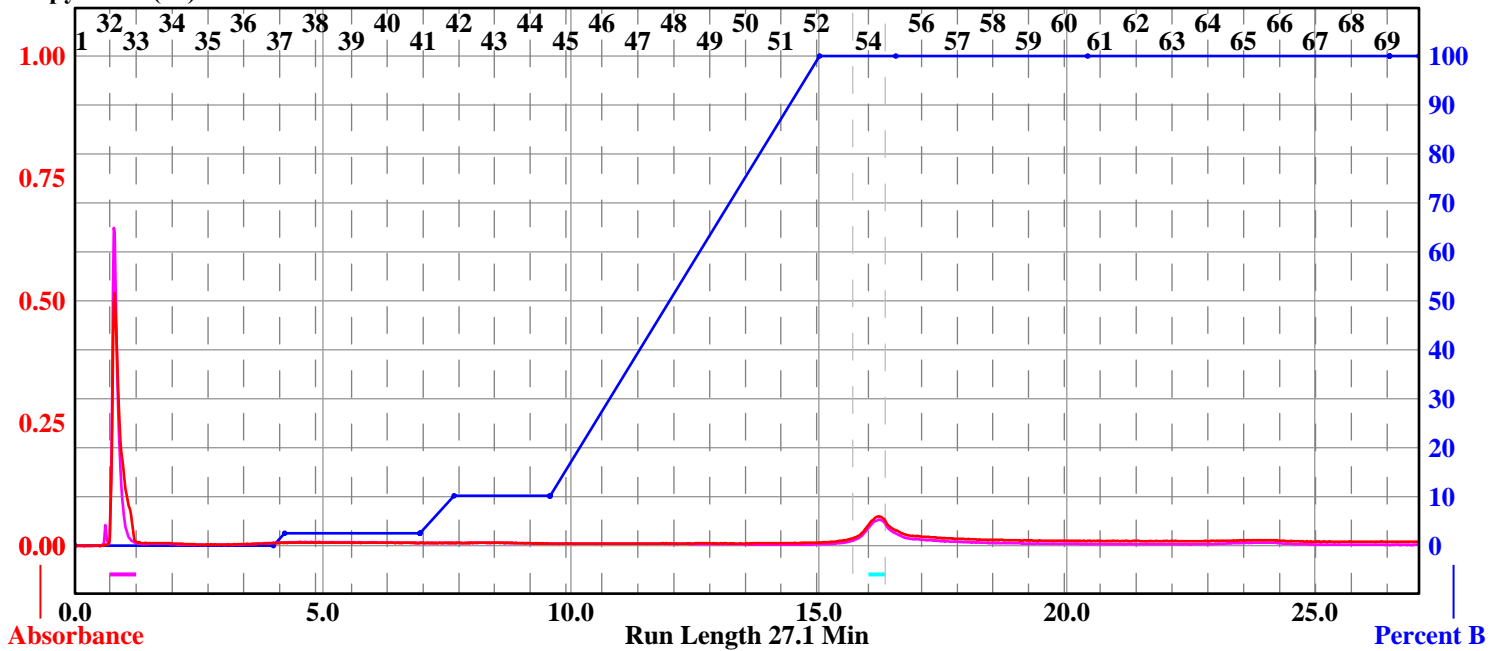
Thursday 18 July 2019 04:29PM

RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A2 dichloromethane
 Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
 Non-Peak Tube Volume: Max.
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm



Run Notes: 6,6'-bis-[5,6-bis(4-(3-methylbutyl)phenyl)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (14)



Rack A				
71	72	73	74	75
70	69	68	67	66
61	62	63	64	65
60	59	58	57	56
51	52	53	54	55
50	49	48	47	46
41	42	43	44	45
40	39	38	37	36
31	32	33	34	35
30	29	28	27	26
21	22	23	24	25
20	19	18	17	16
11	12	13	14	15
10	9	8	7	6
1	2	3	4	5

16 mm x 100 mm Tubes

Peak #	Start Tube	End Tube
1	A:32	A:32
2	A:54	A:54

Duration	%B	Solvent A	Solvent B
0.0	0.0	A2 dichlorometha	B1 ethyl acetate
4.0	0.0	A2 dichlorometha	B1 ethyl acetate
0.2	2.5	A2 dichlorometha	B1 ethyl acetate
2.7	2.5	A2 dichlorometha	B1 ethyl acetate
0.0	2.5	A2 dichlorometha	B1 ethyl acetate
0.7	10.2	A2 dichlorometha	B1 ethyl acetate
1.9	10.2	A2 dichlorometha	B1 ethyl acetate
0.0	10.1	A2 dichlorometha	B1 ethyl acetate
5.4	100.0	A2 dichlorometha	B1 ethyl acetate
1.5	100.0	A2 dichlorometha	B1 ethyl acetate
...

Figure S18.

Sample: GDW-B-197-1

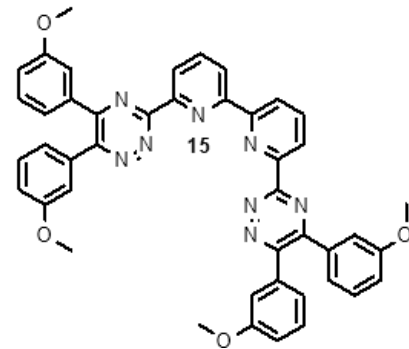
Rf 200

Thursday 31 January 2019 01:53PM

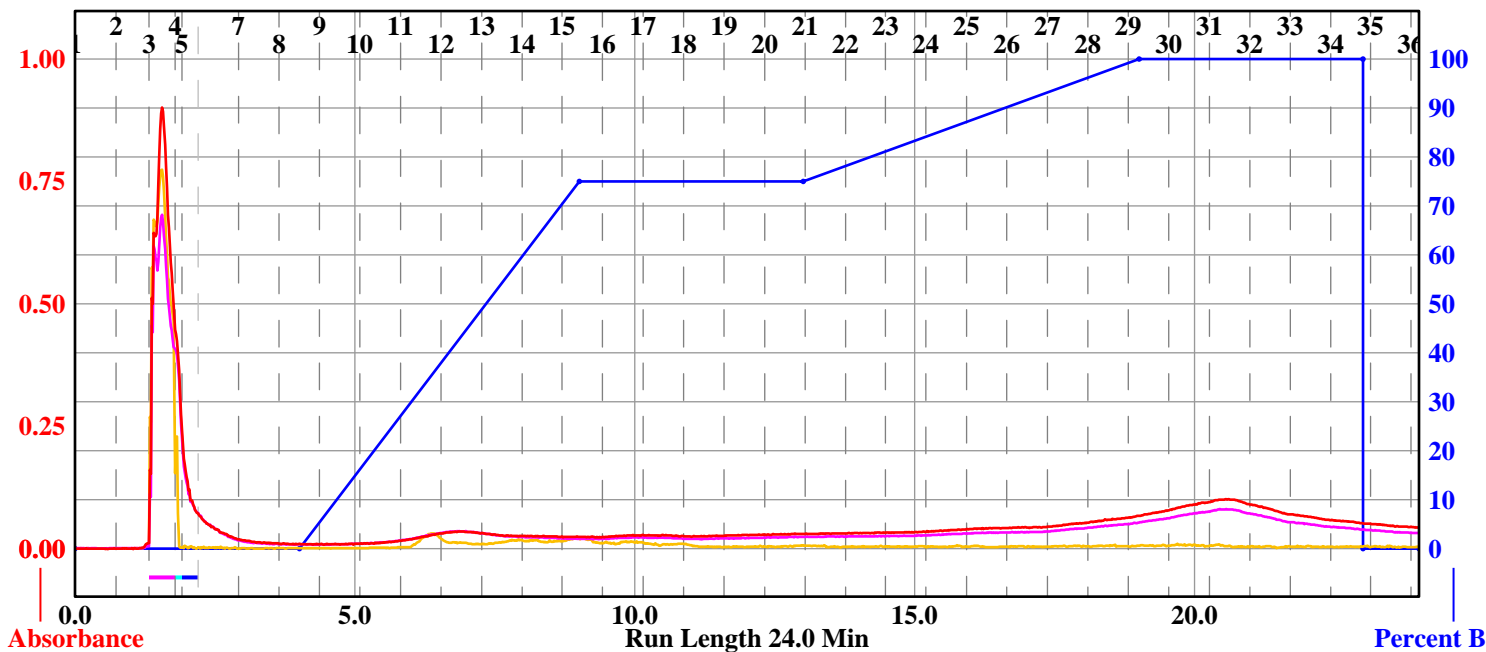
4x Column: 3
 RediSep Column: Silica 4g
 Flow Rate: 18 ml/min
 Equilibration Volume: 33.6 ml
 Initial Waste: 0.0 ml
 Air Purge: 0.5 min
 Solvent: A1 hexane
 Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
 Non-Peak Tube Volume: Max.
 Loading Type: Solid
 Wavelength 1 (red): 254nm
 Peak Width: 30 sec
 Threshold: 0.20 AU
 Wavelength 2 (purple): 280nm

All Wavelength (orange): 200-300nm
 Peak Width: 30 sec
 Threshold: 0.20 AU



Run Notes: 6,6'-bis-[5,6-bis(3-methoxy)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (15)



Rack A				
71	72	73	74	75
70	69	68	67	66
61	62	63	64	65
60	59	58	57	56
51	52	53	54	55
50	49	48	47	46
41	42	43	44	45
40	39	38	37	36
31	32	33	34	35
30	29	28	27	26
21	22	23	24	25
20	19	18	17	16
11	12	13	14	15
10	9	8	7	6
1	2	3	4	5

16 mm x 100 mm Tubes

Peak #	Start Tube	End Tube
1	A:3	A:3
2	A:4	A:4
3	A:5	A:5

Duration	%B	Solvent A	Solvent B
0.0	0.0	A1 hexane	B1 ethyl acetate
4.0	0.0	A1 hexane	B1 ethyl acetate
5.0	75.0	A1 hexane	B1 ethyl acetate
4.0	75.0	A1 hexane	B1 ethyl acetate
6.0	100.0	A1 hexane	B1 ethyl acetate
4.0	100.0	A1 hexane	B1 ethyl acetate
0.0	0.0	A1 hexane	B1 ethyl acetate
1.0	0.0	A1 hexane	B1 ethyl acetate